FRESHWATER BIOLOGICAL ASSOCIATION
The Ferry House, Ambleside, Cumbria LA22 OLP UK

JOINT RESEARCH PROJECT ON THE AQUATIC ECOTOXICITY OF ORGANO-ALUMINIUM: CHEMICAL REACTIONS

FIRST INTERIM REPORT

by

E. Tipping and C. Woof

Project Leader: E. Tipping
Report Date: August 1988
Report To: Commission of European Communities
Contract No: EV4V.0118.UK(H)
FBA Report Ref. No: WI/215/2
FBA Project No: 215
TFS Project No: T04022-5

SUMMARY

Progress has been made on the following topics:

Chemical modelling of ion-binding by humic substances

A computer model has been developed and is being tested using field data. Preliminary results are encouraging, the root-mean-square difference between observed and predicted concentrations of organically-complexed Al being < 1 μM.

Conditions required for the precipitation of aluminium in surface waters

Experiments with natural and synthetic waters show that the effective solubility product for the precipitation of $Al(OH)_3$ from dilute solution is ca 10^{10} at 25 °C, in the absence of interfering agents. This is some 1½ orders of magnitude greater than that for the commonly assumed controller of solubility, gibbsite. The solubility is highly temperature-dependent and is reduced by sulphate and humic substances. A predictive equation that takes temperature and humic interference into account is offered. It is concluded that for many surface waters, precipitation of $Al(OH)_3$ is unlikely under natural conditions.

Fieldwork

A field study has been initiated, that will provide data for the formulation, testing and refinement of a comprehensive speciation model.

CONTENTS

1. GENERAL INTRODUCTION (Technical Annex)

This research forms part of a cooperative project with the following laboratories:

- SCK/CEN, Mol, Belgium (Prof. O. Vanderborght and Dr J. Vangenechten)
- University of Nijmegan (Prof. Wendelaar Bonga).

The overall goal of the joint research project is to relate the chemical reactions involved in the formation of organo-aluminium complexes under acid conditions to their toxic effects on the physiology of aquatic organisms. Finally, this research is intended to predict toxic effects arising from acidity and aluminium under varying environmental conditions.

Specifically, this project is addressing the following research:

(a) Improvement of chemical model systems for Al-HS interaction developed already under contract ENV-865-UK (H). Parameters for Al complexation by several humic fractions will be obtained, and the general applicability of the results assessed. In order to be able to predict H^+/Al^{3+} exchange, and to take ionic strength into account, a polyelectrolyte model will be chosen (Tipping et al. 1988a). The required data will be obtained from potentiometric measurements on isolated humics.

(b) The formation of polymeric hydrolysis products of Al will be studied using kinetic analysis methodology developed under contract ENV-865-UK (H). Work will be done in the laboratory and in the field and will include mixing experiments. Effective solubility products for polymeric species will be estimated. As well as enabling Al speciation to be predicted, the findings should be useful in predicting the removal of soluble Al from waters.

(c) The interaction of Al with natural particulate matter will be studied by exposing particles from natural waters and sediments to varying concentrations of Al and acid or base, and measuring concentrations of soluble Al and pH. Possible ways of modelling the interactions will be explored. The findings will allow the role of particles in Al speciation to be assessed and will give information about the control of soluble Al concentrations.

From these studies it should be possible to produce a quantitative model for Al speciation in acid surface waters that has been validated by field measurements. It will then be possible to predict the distribution of Al among the various possible forms, given pH and total concentrations of Al, F, SO_4, humic substances and particulates.

As well as providing much-needed information on the behaviour of Al in natural waters, the results will be useful in the design and interpretation of physiological experiments and in relating results of weathering studies to field conditions.

2. CHEMICAL MODELLING OF ION-BINDING BY HUMIC SUBSTANCES

2.1 Humic complexation model III: a mechanistic description of the interactions of humic substances with Al^{3+}, $AlOH^{2+}$, H^+ and Ca^{2+}.

Model II, described in a previous report to the Commission (contract ENV-865-UK (H)) was reasonably successful at simultaneously describing Al^{3+} and H^+ binding by the isolated humic fraction used in preliminary laboratory studies, but it proved too restricted to be applied to other humic samples. With the aid of an automatic titration apparatus, data were obtained to test an improved model (model III) that incorporates both humic binding-site heterogeneity and macroionic effects. Data were obtained for humic samples isolated from a stream at Lochard Forest (Central Region, Scotland), from Penwhirn Reservoir (Galloway, Scotland) and from the sediment of Mosedale Beck (Cumbria, England). The samples are referred to as LFHS, PRHS (fractions A and B) and MBHA respectively. Full details of this study are given in Tipping et al. (1988a).

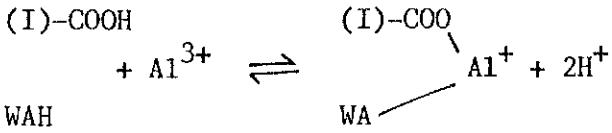
2.1.1 Formulation of model III

The HS are assumed to be macroions with two types (I and II) of carboxyl groups having pK's < 7, together with other groups (weaker COOH, phenolic OH) with pK's > 7, although the latter may exchange a proton for a metal ion at pH < 7. Metal complexation is assumed to be at bidentate sites (cf. Gamble et al., 1980), but these are restricted to type A (consisting of a type I and a type II carboxyl), type BI (type I carboxyl, 'weak acid') and type BII (type II carboxyl, 'weak acid'). We therefore have the following reactions for the humic-Al^{3+}-H^+ system:

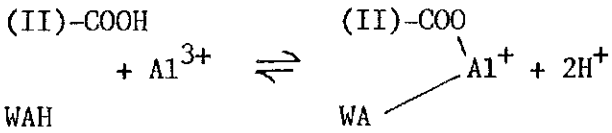
$$(I)\text{-}COOH \rightleftharpoons (I)\text{-}COO^- + H^+ \qquad (2.1)$$

$$(II)\text{-}COOH \rightleftharpoons (II)\text{-}COO^- + H^+ \qquad (2.2)$$

$$\begin{matrix}(I)\text{-}COOH \\ \quad + Al^{3+} \\ (II)\text{-}COOH\end{matrix} \rightleftharpoons \begin{matrix}(I)\text{-}COO \\ \quad\quad Al^+ + 2H^+ \\ (II)\text{-}COO\end{matrix} \qquad (2.3)$$



(2.4)



(2.5)

where 'WAH' indicates a protonated 'weak acid' group. In order to include the possibility of the binding of $AlOH^{2+}$ we add the reaction

$$Al^{+} + H_2O \rightleftharpoons Al\text{-}OH + H^{+} \qquad (2.6)$$

Reactions (2.1) and (2.2) are characterized by the intrinsic dissociation constants $\underline{K}_I$ and $\underline{K}_{II}$. The same intrinsic equilibrium constant $\underline{K}_{Al}$ is assumed to apply to reactions (2.3), (2.4) and (2.5). Reaction (2.6) has the intrinsic equilibrium constant $\underline{K}_H$. Analogous equations can be written for humic-Ca^{2+}-H^{+} systems, but omitting equation (2.6).

We assume that there are $\underline{n}/2$ type I and $\underline{n}/2$ type II carboxyl groups per gHS. The content of weak acid groups is given by the total acidity ($\underline{Ac}$) minus the content of COOH groups. There are thus $\underline{n}$-($\underline{Ac}$/2) type A metal complexation sites per gHS, ($\underline{Ac}$-$\underline{n}$)/2 type BI sites and ($\underline{Ac}$-$\underline{n}$)/2 type BII sites, giving a total binding capacity of $\underline{Ac}$/2 moles/gHS. Electrostatic effects are incorporated in the usual way (Tanford, 1961) by using the expression $e^{-2\underline{wzZ}}$ to modify the intrinsic equilibrium constants: here $\underline{z}$ is the charge on the complexing ion and $\underline{Z}$(eq/g) that on the HS, while $\underline{w}$(gHS/eq) is the electrostatic interaction factor. For example the fractional dissociation of type I COOH groups is given by

$$f_I = \frac{K_I\, e^{2wZ}/a_{H^+}}{1 + K_I e^{2wZ}/a_{H^+}} \qquad (2.7)$$

where $\underline{a}_{H+}$ is the activity of H^{+}.

The electrostatic interaction factor $\underline{w}$ depends on the ionic strength and for 2 of the 4 humic samples studied was found to depend also on $\underline{Z}$. On the basis of preliminary calculations we adopt the following empirical expression for $\underline{w}$:

$$w = P(\log_{10} I)e^{(Q * |Z|)} \qquad (2.8)$$

where P and Q are constants (both negative), I is the ionic strength and |Z| is the modulus of Z. Inspection of equation (2.8) shows that w = 0 for an ionic strength of 1M, i.e. electrostatic effects are assumed to be completely abolished under these conditions. Ephraim et al. (1986) presented experimental evidence to show that this is indeed the case. Since Q is negative it is seen that w decreases with Z: this is common behaviour for macroions and is taken to indicate the expansion of the macromolecule due to charge-charge repulsion as the degree of ionisation increases (Tanford, 1961). The same relationship between w and Z is assumed whether or not metal ions are bound.

The model thus has 8 parameters (n, Ac, K_I, K_{II}, K_{Al}, K_H, P and Q) one of which, Ac, can be measured directly. The remaining 7 were determined from acid-base titration data by non-linear least squares fitting. In brief, n, K_I, K_{II}, P and Q were estimated from data obtained in the absence of metal, and with these values fixed, K_{Al} and K_H (or just K_{Ca}) were estimated from data obtained in the presence of metal. Hydrolysis reactions of Al, involving the species Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$ were taken into account using the equilibrium constants of May et al. (1979). Activity coefficients were calculated with the extended Debye-Hückel equation.

For complexation of H^+ and Al species the present model (model III) differs from model II in that it incorporates two types of humic COOH group, allows the ratio of weak acid groups to COOH groups to vary, has an expression for the variation of w with I and Z, uses only one equilibrium constant for Al^{3+} binding and incorporates the binding of $AlOH^{2+}$. Model II has 5 parameters for a given ionic strength, whereas model III has 8 parameters but applies to all ionic strengths.

2.1.2 Parameters for model III

Parameters have been derived for 4 samples of humic substances, on the basis of laboratory acid-base titration data. These are summarised in Tables 2.1 and 2.2. Originally it had been planned to perform the titration experiments under the current contract, but it has proved possible to carry out most of the work ahead of time. It is thus possible to subject model III to more extensive field testing (see next section). As it stands, the model is satisfactory for describing the titration data, and for predicting Al and Ca binding by isolated HS (Tipping et al. 1988a).

2.1.3 Testing model III with field data

Preliminary testing of the model has been carried out using field data from 8 sites (114 samples) in N.W. Europe and N. America, by comparing observed and predicted concentrations of [Al_m-org] - the concentration of organically complexed monomeric Al. Aluminium speciation calculations were carried out taking into account the complexation of Al^{3+} by OH^-, F^-, SO_4^{2-} and HS, but ignoring any possible competition by Ca^{2+}. Parameter values of LFHS were employed, this sample being the most typical of HS in natural waters. The temperature of all the field samples was assumed to be 10°C. Equilibrium constants for the inorganic complexation reactions were converted from 25°C values by means of the enthalpies listed by Tipping et al. (1988b). For the LFHS, all parameters except K_H were assumed to be temperature-independent. Clearly Ac and n do not vary with temperature, while theoretical expressions for the electrostatic free energies of macroions (Tanford, 1961) indicate that P and Q would tend to be temperature-independent. Enthalpies of proton- and metal-binding to -COOH groups are close to zero (e.g. Martell and Smith, 1977) so that reactions (2.1)-(2.3) can be expected to have similar equilibrium constants at 10 and 25°C. In the absence of literature values we also assume that H^+/Al^{3+} exchange reactions at 'weak acid' sites (mainly phenolic OH) - see equations (2.4) and (2.5) - have enthalpies close to zero. A value of K_H at 10°C (9.4×10^{-7}) was estimated using the enthalpy for the hydrolysis of Al^{3+}, i.e. 12.8 kcal mol^{-1} (Couturier et al., 1984).

Speciation calculations using the LFHS parameters shown in Tables 2.1 and 2.2 gave overestimates of [Al_m-org]. The mean residual ($[Al_m\text{-org}]_{calc} - [Al_m\text{-org}]_{meas}$) was 1.0 µM Al, the root-mean-square residual was 1.4 µM. An improvement was made by adjusting the values of Ac and n, keeping the ratio n/Ac constant. For the data as a whole a value of Ac of 5.7×10^{-3} eq/gHS gave the best (least squares) agreement, with a mean residual of 0.1 µM Al and a root-mean-square residual of 0.8 µM. Optimised values of Ac (Ac_{opt}) were also calculated for results from individual sites (Table 2.3). Comparison with results for model I (see report ENV-865-UK (H)) shows that model III gives slightly better predictions for 3 of the field locations, slightly worse for 3, and the same for the remaining two. Overall a slight improvement is obtained with model III.

In the current work, further field data will be obtained, from 6 sites in Pennine region of England, and from sites (bog-lakes) in Belgium and the Netherlands. Sampling and analysis of the Pennine sites is underway: 100

samples have been taken and analysed for temperature, pH, total Al, total monomeric and organic monomeric Al, major ions, dissolved organic carbon, optical absorbance, total fluoride, iron, suspended load and conductivity. This sampling programme is planned to continue until May 1989, yielding approx. 220 samples in all, covering a whole year. The Belgian and Dutch sites will contribute a further ca. 50 samples. Thus a sufficiently large data set should be available for optimising the model parameters.

Model development will continue with attention being paid to the influence of the electrical double layer of the humic substances. Preliminary calculations show that, owing to its high charge, Al^{3+} may accumulate in the diffuse part of the double layer when the humics are negatively charged (their usual state) and the ionic strength is low. This may have important implications for Al speciation.

Table 2.1 Parameters for model III, derived from metal-free titrations. Figures in brackets are 2x asymptotic standard error.

	LFHS	MBHA	PRHS-A	PRHS-B
10^3Ac (eq/gHS)	9.73	4.80	5.85	8.10
10^3n (eq/gHS)	5.46(0.12)	2.51(0.06)	2.98(0.08)	4.95(0.04)
10^3K_I	4.85(0.54)	2.11(0.36)	2.38(1.16)	5.10(3.78)
10^5K_{II}	6.97(1.84)	3.42(1.56)	4.95(1.38)	2.63(0.62)
-P	120(20)	1680(240)	810(220)	12(12)
-Q	0	870(120)	410(140)	0
mr*	-0.01	0.00	0.00	-0.01
rmsr**	0.05	0.06	0.03	0.08
r***	0.998	0.999	0.999	0.995
no. of data	80	35	23	47

Table 2.2 Parameters for model III, derived from titrations with Al present. Figures in brackets are 2x asymptotic standard error.

	LFHS	MBHA	PRHS-A	PRHS-B
10^4K_{Al}	2.19(0.50)	1.65(0.28)	2.97(1.84)	4.43(0.72)
10^5K_H	0.27(0.28)	4.41(1.9)	3.24(2.14)	0.48(0.24)
mr*	-0.03	-0.01	-0.01	0.00
rmsr**	0.09	0.09	0.09	0.05
r***	0.992	0.983	0.972	0.996
no. of data	59	60	24	42
10^7K_{Ca}	1.46(1.48)	1.63(2.34)	-	-
mr*	0.01	0.03	-	-
rmsr**	0.14	0.14	-	-
r***	0.969	0.974	-	-

* mean residual (pH units)

** root mean square residual (pH units)

*** correlation coefficient for untransformed pH values

Table 2.3 Application of model III to field data.

Location	no. of samples	range of $[Al_m\text{-org}]$, μM	$10^3 Ac_{opt}$	residuals* mean	rms
R. Duddon	9	0.1–1.7	7.8	-0.1	0.7
Falls Brook	19	0.9–9.0	6.4	0.4	1.1
L. Hovvatn	11	2.1–2.7	3.2	0.1	0.3
Paint Lake inflow	14	2.0–4.3	5.3	0	0.4
Plastic Lake inflow	21	1.3–9.7	7.1	0.1	0.5
Plastic Lake outflow	20	0.4–2.7	5.5	0	0.1
R. Swale	10	0.8–5.8	4.1	0	0.5
Whitray Beck	10	1.6–5.1	5.3	-0.1	1.1
All	114	0.1–9.7	5.7	0.1	0.8

* $[Al_m\text{-org}]_{calc} - [Al_m\text{-org}]_{meas}$, μM

3. CONDITIONS REQUIRED FOR THE PRECIPITATION OF ALUMINIUM IN SURFACE WATERS

3.1 Introduction

In waters of pH ≤6, aluminium in solution is commonly close to saturation with respect to oxide phases or other solid forms (Johnson et al., 1981; Nordstrom, 1982; Driscoll 1985). Precipitation of the metal might therefore be brought about by quite small changes in conditions (e.g. pH, concentrations of Al complexing agents, temperature), as might occur when waters of different composition mix, or when groundwater high in CO_2 is exposed to the atmosphere (Norton & Henriksen, 1983). Such precipitation could be important for several reasons:

(a) Freshly formed polymeric hydrolysis products are thought to be toxic to fish and other organisms (Baker 1982; Dickson, 1983).

(b) The precipitate would be the phase controlling the solution chemistry of Al, in terms of both removal and remobilisation. Also, it could adsorb trace metals, organic matter and phosphate, thereby exerting further control over solution chemistry (Driscoll, 1985).

(c) Polymeric hydrolysis products can substantially modify the surface chemistry and colloid stability of suspended particulate matter (as is well known from water-treatment practice) thereby influencing adsorption and transport processes.

It is therefore desirable to know under what circumstances precipitation of Al in natural waters may occur. At present, however, predictions can be made only on the basis of solubility products for pure phases that have not been formed under conditions relevant to natural waters (see e.g. Bache, 1986). The work described here was carried out with the aim of defining more precisely the natural conditions necessary for precipitation, focussing on reactions occurring in dilute solutions of pH 4-6, over short time-periods and at temperatures in the range 0-25°C.

3.2 Precipitation in the $Al(NO_3)_3$-$NaHCO_3$-$NaNO_3$ system

Laboratory experiments were carried out in which an $Al(NO_3)_3$ solution was mixed with an equal volume of a bicarbonate solution; this procedure avoids the risk of high local concentrations of strong base during mixing. The pH values after mixing were in the range 5.2-6.1. Precipitation was assumed definitely to have occurred when $[Al_m]$ after mixing was <90% of the total Al.

The precipitation reaction was assumed to be either

$$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3\ (s) + 3H^+ \qquad (3.1)$$

or

$$Al^{3+} + 2H_2O \rightleftharpoons AlOOH\ (s) + 3H^+ \qquad (3.2)$$

For both, a solubility product $\underline{K}_S$, in the form $\underline{a}_{Al}3+/(\underline{a}_{H}+)3$ is appropriate. Measurements of $[Al_m]$ and pH were made over a 1h period. During this time both varied, pH invariably rising, $[Al_m]$ falling. From speciation calculations for Al_m, $\underline{a}_{Al}3+$, the activity of Al^{3+}, was estimated and ion activity products (IAP'S) were calculated. Values of $\log_{10}$IAP varied by ≤ 0.1 during the individual experiments, and although there was often a systematic change with time, both increases and decreases were found to occur, so there was no reason to conclude that solubility was markedly time-dependent.

It is convenient to express the temperature dependence of $\underline{K}_S$ as follows:

$$\log_{10}\underline{K}_S(\underline{T}) = \log_{10}\underline{K}_S(\underline{T}^*) + \frac{\Delta H}{\underline{R}\log_e 10}\left\{\frac{1}{\underline{T}^*} - \frac{1}{\underline{T}}\right\} \qquad (3.3)$$

where $\underline{T}$ is the temperature of interest (in deg.K), $\underline{T}^*$ a reference temperature, ΔH the enthalpy change and $\underline{R}$ the gas constant. In writing equation (3.3) we assume that $\Delta \underline{H}$ for the reaction does not vary with temperature. This assumption is borne out by the good linearity ($r = 0.995$) found when values of $\log_{10}\underline{K}_S$ were plotted against $1/\underline{T}$ for results (111 determinations of $\log_{10}\underline{IAP}$) in the temperature range 2–20 °C. We find $\Delta \underline{H} = -30.5(\pm 0.6)$ kcalmol^{-1} and $\log_{10}\underline{K}_S(298K) = 9.99\ (\pm 0.12)$, uncertainties being expressed as 2 x standard error. The enthalpy value is somewhat greater than that of -21.3 kcalmol^{-1} for gibbsite (Couturier *et al*. 1984). The value of $\log_{10}\underline{K}_S$ (298K) is larger than those of 8.11 and 8.77 found for synthetic and natural gibbsite respectively by May *et al*. (1979) and also exceeds the value of 9.35 given for microcrystalline gibbsite by Hem and Roberson (1967): this would be expected since the precipitate formed in our experiments was fresh and presumably very poorly crystalline. Nonetheless the value of $\log_{10}\underline{K}_S$ (298K) reported here is less than that of 10.8 for amorphous $Al(OH)_3$ 'given with reserve' by Feitknecht and Schindler (1963); the latter value refers to amorphous precipitates in solutions of dilute acid and alkali, conditions less relevant to precipitation reactions in most natural waters than those employed in the present work.

The results for the precipitate formed in this system, which we shall refer to as the 'simple medium phase', provide a useful yardstick against which to judge IAP values for more complex media, i.e., from now on, SI values are calculated relative to the K_S for the simple medium phase.

3.3 Ion activity products for field samples

Fig. 3.1 shows a plot of SI vs. pH for samples taken from the River Swale, from Whitray Beck, and from several streams in the catchment of the River Duddon. The first conclusion to be drawn from the results is that $a_{Al}3+$ is not controlled simply by the solubility of an Al oxyhydroxide phase in these waters, since SI varies by 6 orders of magnitude, and is strongly dependent on pH. In none of the samples is saturation with respect to the simple medium phase reached. Degrees of saturation of the field samples with respect to aluminosilicates and basic aluminium sulphates were tentatively assessed by comparison of IAP's with the 25°C solubility products compiled by Bache (1986). Some samples were calculated to be oversaturated with respect to kaolinite, halloysite, pyrophyllite and the 'reversible metastable aluminosilicate' of Paces (1978), and it is therefore conceivable that more amorphous analogues of these phases are forming in the streamwaters. However the SI values showed definite pH-dependences suggesting that none of these phases was being formed in the streamwaters. Further evidence against their formation is the lack of influence of $Si(OH)_4$ on Al precipitation in laboratory experiments. Although Duddon waters are invariably oversaturated with respect to basaluminite and alunite the formation of these phases under streamwater conditions (low temperature, short residence time) is highly unlikely (Nordstrom, 1982). The most likely basic aluminium sulphate to form is jurbanite (Nordstrom, 1982) but all the samples were undersaturated with respect to this mineral. We conclude that there is no evidence for the precipitation of either alumino-silicates or basic aluminium sulphates in any of the samples analysed.

Further study of the degree of saturation of Al oxide in natural waters was confined to streams in the Duddon catchment, firstly because values of $[Al_m]$ tended to be highest for these waters, and secondly because they have lower concentrations of Al-complexing agents (especially humic substances), making speciation calculations more reliable and solution compositions closer to the simple bicarbonate medium. For these samples (79 in all), Al speciation was estimated without measuring $[Al_m\text{-org}]$ directly; instead the organic complexation model III was used. Values of SI are plotted against pH in Fig.

3.2. It is apparent that in none of the samples examined is saturation reached with respect to the 'simple medium phase'. Ion activity products for the other phases considered above were similar to those for the samples in which $[Al_m\text{-org}]$ was measured directly.

3.4 Mixing experiments with natural water samples

The above results suggest that precipitation of an Al oxyhydroxide with the same solubility as the 'simple medium phase' occurs rarely, if ever, in the natural waters studied. In order to ascertain conditions actually required for precipitation, a series of experiments was carried out in which samples of streams in the Duddon catchment were mixed together. Results for those experiments in which precipitation of Al took place are given in Table 3.1. It appears that when formation of an insoluble Al phase (presumed to be an oxyhydroxide) occurs, the SI with respect to the 'simple medium phase' is on average -0.3 (with temperature taken into account). This small value means that the phase precipitated from the Duddon waters is only slightly less soluble than that formed in the simple medium experiments. This confirms our conclusion that Al precipitation from Duddon waters is an unlikely event.

3.5 Precipitation of Al in the presence of F^-, SO_4^{2-}, $Si(OH)_4$, humic substances and Ca^{2+}

In view of the slightly lower solubility of the Al phase precipitated from mixtures of Duddon waters, compared to that of the 'simple medium phase', the effects on precipitation of some of the solutes present in the streamwaters were studied. It was found that F^- and $Si(OH)_4$ are without effect at the concentrations used (typical of acid natural waters). Sulphate, however, lowers the solubility of the Al phase at pH ≥5.8 (10°C). Thus at pH 6 the apparent solubility product is decreased by up to 0.3 log units in the presence of 50 or 200μM SO_4^{2-}. Since the concentration of SO_4^{2-} in the Duddon waters was 30–50μM, it is quite possible that SO_4^{2-} was important in determining the solubility of the Al phase precipitated from the natural water mixtures. In the laboratory mixing experiments the solutions were all over-saturated (SI 4 to 7) with respect to basaluminite and under-saturated (SI -2.1 to -0.4) with respect to jurbanite, assuming the K_S values at 25°C for these minerals to apply at 10°C. As already discussed, basaluminite is unlikely to form under these dilute, low-temperature conditions. The SI's with respect to jurbanite are sufficiently close to zero to make its precipitation a

possibility, however the values decreased systematically with pH and also depended on $[SO_4^{2-}]$. Thus the most plausible explanation for the effect of SO_4^{2-} on Al solubility is that it influences the formation of an Al (oxy)hydroxide phase.

The laboratory mixing experiments with inorganic solutes were carried out at 10°C, in order to simulate natural conditions. For practical reasons, however, experiments with humic substances (HS) were performed at 25°C. The reasons were, first, that parameter values for organic complexation model III were available to describe Al binding by the HS used (Lochard Forest HS) at 25°C (Tipping et al., 1988a), and second, that at the higher temperature, precipitation of Al oxyhydroxide occurs at lower pH values, where Al-humic complexation is less pronounced and estimated values of a_{Al}^{3+} therefore more reliable.

It was found that HS at typical natural concentrations lower the solubility of Al appreciably. The apparent $\log_{10} K_S$ for the Al phase was found to decrease systematically with [HS] in the range studied, so that at 6.6 mgHS/l it is some 1.5 log units less than in the humic-free system. For Duddon streams [HS] is ca. 1 mg/l, at which concentration an apparent K_S 0.2–0.3 log units less than in the humic-free system would be expected, and is indeed observed, as discussed above.

It is not possible to deduce the mechanism(s) whereby SO_4^{2-} and HS reduce the solubility of Al solely on the basis of the present results. The fact that both solutes are known to adsorb to Al oxides (Stumm et al., 1980; Davis, 1982) suggests that a surface effect may be operating : perhaps the neutralisation of surface positive charge by interaction with the anions allows further Al^{3+} to approach the forming precipitate more readily (Snodgrass et al., 1984). However in the case of HS matters are more complicated, because precipitation of Al can occur in the presence of HS at pH values too low for it to do so in their absence, so that prior formation of an Al oxyhydroxide phase is apparently not necessary for HS to exert their effect.

The possible influence on Al precipitation of Ca^{2+}, the major divalent cation in most acid waters, was investigated by including 50 or 100μM $Ca(NO_3)_2$ in the experimental solutions. Calcium additions were made to the simple bicarbonate medium, and to solutions containing 50μM SO_4^{2-} or 2.7 mg/l HS. No significant changes in the values of SI were found.

3.6 Predicting the influence of humic substances on the precipitation of Al in surface waters

Equation (3.3) provides a means of taking temperature variation into account, but further information on the mechanism(s) of solubility reductions by SO_4^{2-} and HS, together with data over a wider range of humic concentrations, is required in order to make proper quantitative predictions of the influence of these anions on Al solubility. In the meantime, however, a possible approach is to assume that the effects of temperature and the anions are additive with respect to $\log_{10}\underline{K}_S$. To simplify further we assume (1) that the effect of HS will predominate over that of SO_4^{2-} (this is reasonable in view of the relatively small influence of SO_4^{2-} at natural concentrations), (2) that the decrease in $\log_{10}\underline{K}_S$ due to the HS bears a linear relationship to [HS] in the range 0–7 mg HS/1, and (3) that any HS incorporated into the Al (oxy)hydroxide precipitate represents only a small proportion of the total HS present. We can then write:

$$\log_{10}\underline{K}_S^{\underline{eff}}(\underline{T},[HS]) = \log_{10}\underline{K}_S(\underline{T}^*) + \frac{\underline{\Delta H}}{\underline{R}\log_e 10}\left\{\frac{\underline{1}}{\underline{T}^*} - \frac{\underline{1}}{\underline{T}}\right\} + \underline{b}[HS] \quad (3.4)$$

where $\underline{b}$ is a constant, estimated to be ~0.25 1/mgHS from the results discussed in section 3.5, the superscript $\underline{eff}$ indicates an effective value, and [HS] is a total concentration. It should be emphasized that the equation can only be valid for [HS]<7 mg/1; it is improbable that $\log_{10}\underline{K}_S^{\underline{eff}}$ will continue its linear decrease at higher [HS], therefore extension of equation (3.4) to a wider range of [HS] would require the replacement of the term $\underline{b}$[HS] with a more complicated function. (It is also quite possible that $\underline{b}$[HS] or its replacement are themselves temperature-dependent, complicating things further).

Equation (3.4) was used to calculate $\log_{10}\underline{K}_S^{\underline{eff}}$ for different temperatures and humic concentrations (Fig. 3.4). It is found to vary considerably, from 12 for low temperature, low humic waters, to 9 for warm waters with ca. 5 mgHS/1. The variation in the calculated values suggests that assessments of the degree of under- or over-saturation of solutions with respect to Al (oxy)hydroxide should be made with caution: the use of solubility products for pure phases at 25 °C (e.g. Johnson et al., 1981; Driscoll, 1985) may give estimates of SI that are uncertain by 1 to 2 $\log_{10}$ units corresponding to 10- to 100-fold uncertainties in Al solubility.

We have seen from the results of mixing experiments (Table 3.1) that the measured value of $\log_{10}K_S^{eff}$ for Duddon waters is ca. 0.3 $\log_{10}$ units lower than that for the simple medium phase (this is consistent with equation (3.4)), and that the waters are undersaturated with respect to Al (oxy)hydroxide. It is now appropriate to re-examine the results for the River Swale and Whitray Beck. Of the 20 samples from these two waters, 7 had [HS]<7 mg/l and so equation (3.4) can be applied. In only one of the samples, from Whitray Beck, was a positive effective SI obtained (+0.8). The conclusion remains, therefore, that the precipitation of Al from the natural waters examined in this work is an unlikely event.

3.7 Further plans

The possible precipitation of Al in natural waters will be tested for using the field data that is currently being collected (section 2.1.3). In the 'over-acidified' high-sulphate waters of Belgium and the Netherlands, ion activity products with respect to jurbanite ($Al(OH)SO_4$) will be calculated to test for solubility control by this mineral. The current findings should prove useful in designing physiological experiments in the collaborating laboratories.

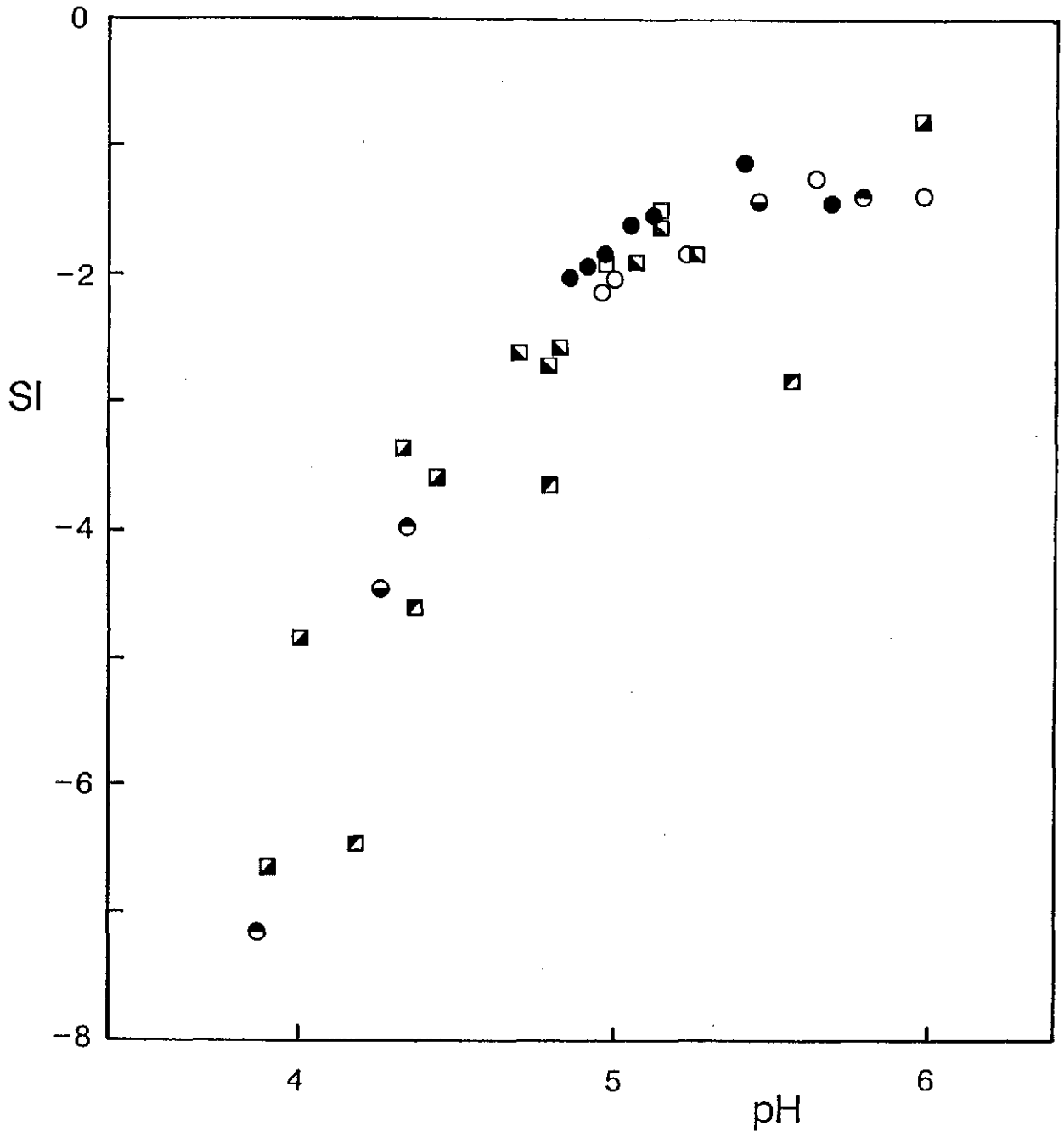


Fig. 3.1 Values of the saturation index (SI) with respect to the "simple medium phase" (Al (oxy)hydroxide) for natural water samples. The symbols ○, ● and □ refer to the River Duddon, ◪ and ◩ to the River Swale ◒, ◓ and ◪ to Whitray Beck.

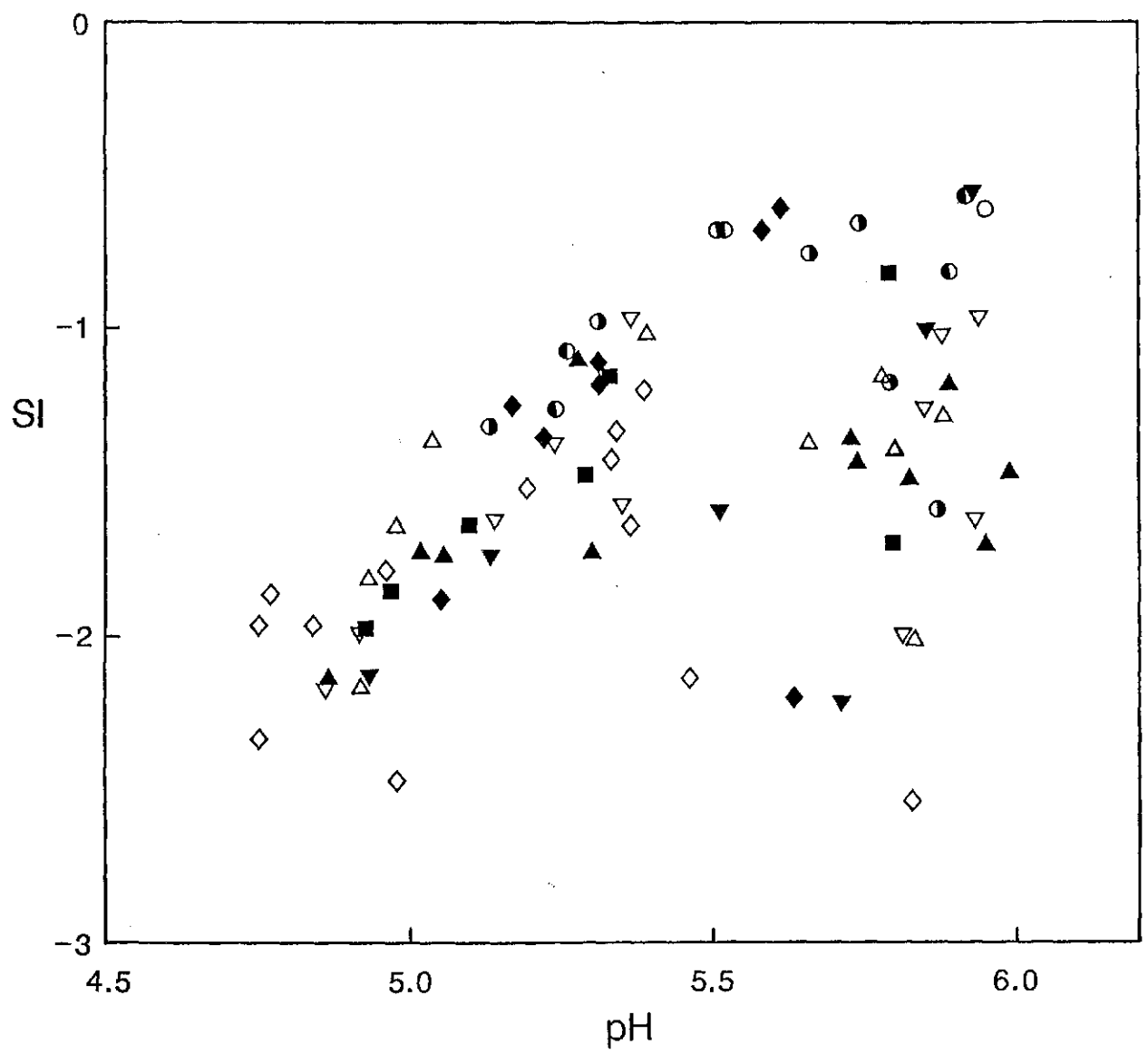


Fig. 3.2 Values of SI with respect to the "simple medium phase" (Al(oxy)hydroxide) for natural waters of the Duddon catchment, based on speciation calculations using model III. Each symbol represents a different sampling trip.

Table 3.1 Mixing experiments with natural water samples. 'Acid' solutions were from Gaitscale Gill (NGR SD 258021) or Dale Head Gill (NGR SD 239001), 'base' solutions from streams at SD 263002 and SD 266024. Ionic strengths after mixing were 0.0004 - 0.00045 M. A spike of 10μM $Al(NO_3)_3$ was added to the 'acid' solutions in experiments 8, 9, 10, 13, 14, 15. Precipitation occurred in all experiments (final $[Al_m]$ <90% of total Al). Concentrations are in μM, except for HS (mg/l). T_F = total fluoride. Speciations were calculated using organic complexation model III. SI values are relative to the simple medium phase.

expt.	temp.	pH	$[Al_m]$	T_F	$[SO_4^{2-}]$	[HS]	$\log_{10}$IAP	SI
1	14	5.85	2.8	1.7	46	0.9	10.34	-0.51
2	10	5.74	4.9	1.5	36	1.0	10.75	-0.43
3	10	5.93	3.4	1.5	37	1.0	10.77	-0.41
4	20	5.62	3.6	1.5	36	1.0	9.94	-0.43
5	20	5.84	2.1	1.5	37	1.0	9.84	-0.53
6	10	5.73	5.2	1.5	37	1.0	10.70	-0.48
7	10	5.96	3.1	1.5	37	1.1	10.70	-0.48
8	10	5.62	9.1	1.5	37	1.0	10.97	-0.21
9	10	5.80	5.8	1.5	37	1.1	10.96	-0.22
10	10	5.89	4.2	1.5	37	1.2	10.82	-0.36
11	10	5.79	4.4	1.8	42	0.5	10.85	-0.33
12	10	5.99	2.8	1.8	43	0.4	10.91	-0.27
13	10	5.64	9.3	1.8	42	0.5	11.06	-0.12
14	10	5.77	6.1	1.8	43	0.4	11.05	-0.13
15	10	5.92	3.6	1.8	43	0.4	10.96	-0.22

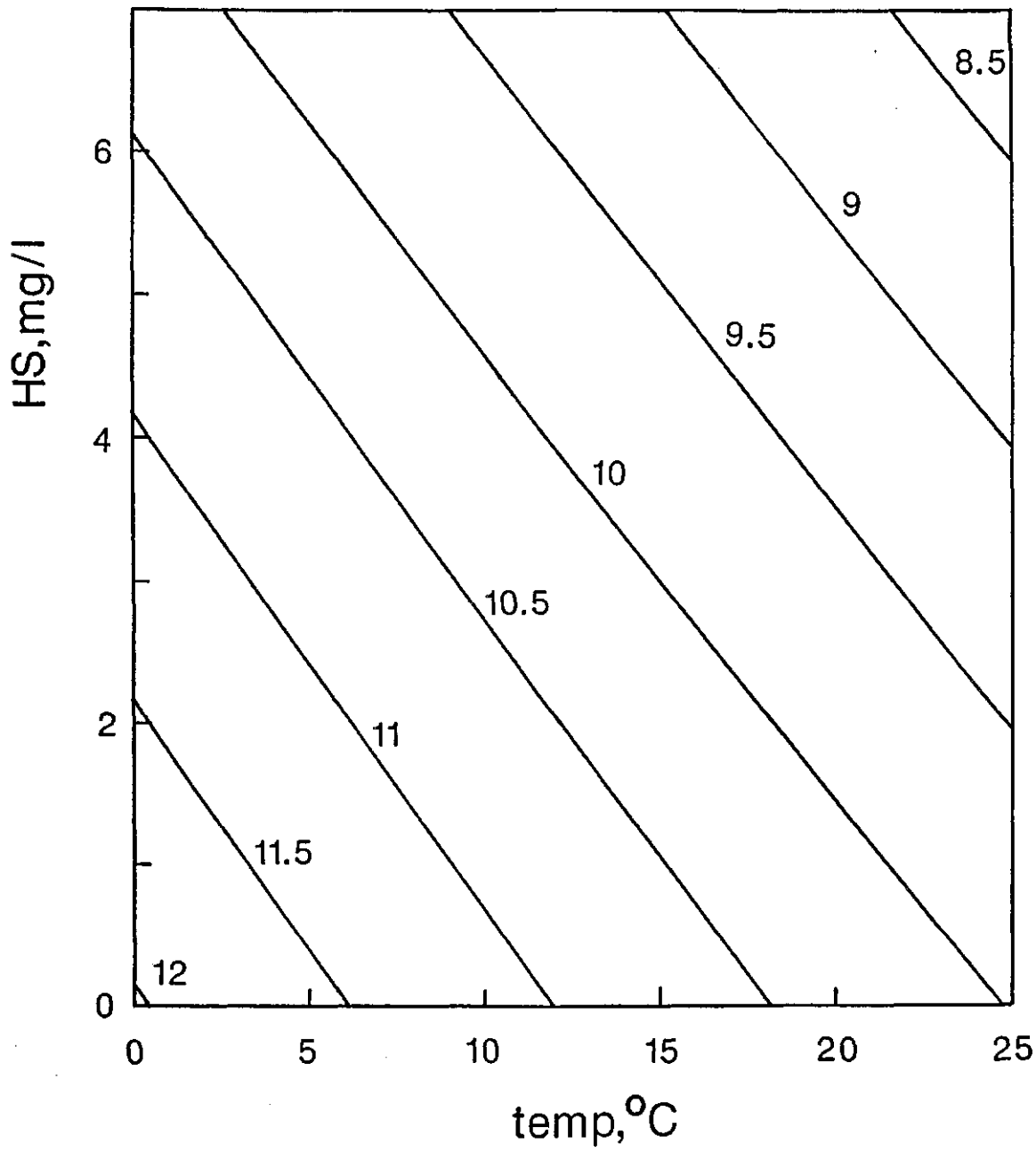


Fig. 3.3 Dependence of the effective solubility product of Al (oxy)hydroxide - $\underline{K}_S^{eff}$ - on temperature and the concentration of humic substances, calculated from equation (3.4). Lines of constant $\log_{10}\underline{K}_S^{eff}$ are shown.

4. INTERACTION OF ALUMINIUM WITH STREAMWATER PARTICULATES

This part of the study has been started with some preliminary laboratory experiments using natural particles from Whitray Beck (Pennines). First results indicate that uptake of Al by particles may be significant at pH > 4.5 and at particle concentrations > 100 mg l^{-1}.

5. ACKNOWLEDGEMENTS

Thanks are due to H. Gardberg for the production of this report, and to J. Manning, M. Ohnstad, P. Walters and the FBA analytical chemists for technical assistance.

6. REFERENCES

Bache, B.W. (1986) Aluminium mobilization in soils and waters, J. Geol. Soc. 143, 699-706.

Baker, J.P. (1982) Effects on fish of metals associated with acidification, in Acid Rain/Fisheries, R.E. Johnson (ed.) Am. Fish. Soc. Bethesda.

Couturier, Y., Michard, G. & Sarazin, G. (1984) Constantes de formation des complexes hydroxydés de l'aluminium en solution aqueuse de 20 à 70°C, Geochim. Cosmochim. Acta 48, 649-659.

Davis, J.A. (1982) Adsorption of natural dissolved organic matter at the oxide/water interface, Geochim. Cosmochim. Acta 46, 2381-2393.

Dickson, W. (1983) Liming toxicity of aluminium to fish, Vattten 4, 400-404.

Driscoll, C.T. (1985) Aluminium in acidic surface waters : chemistry, transport and effects, Environ. Health Perspect. 63, 93-104.

Ephraim, J., Alegnet, S., Mathuthu, A., Bicking, M., Malcolm, R.L. & Marinsky, J.A. (1986) A unified physicochemical description of the protonation and metal ion complexation equilibria of natural organic acids (humic and fulvic acids). 2. Influence of polyelectrolyte properties and functional group heterogeneity on the protonation equilibria of fulvic acid. Environ. Sci. Technol. 20, 354-366.

Feitknecht, W. & Schindler, P. (1963) Solubility constants of metal oxides, metal hydroxides and metal hydroxide salts in aqueous solution, Pure and App. Chem. 6, 130-199.

Hem, J.D. & Roberson, C.E. (1967) Form and stability of aluminium hydroxide complexes in dilute solution, U.S. Survey Water Supply Paper 1827-A, Washington DC.

Johnson, N.M., Driscoll, C.T., Eaton, J.S., Likens, G.E. & McDowell, W.H. (1981) 'Acid rain', dissolved aluminium and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire, Geochim. Cosmochim. Acta 45, 1421-1437.

Martell, A.E. & Smith, R.M. (1977) Critical Stability Constants. Vol. 3. Plenum, New York.

May, H.M., Helmke, P.A. & Jackson, M.L. (1979) Gibbsite solubility and thermodynamic properties of hydroxyaluminium ions in aqueous solutions at 25°C, Geochim. Cosmochim. Acta 43, 861-868.

Nordström, D.K. (1982) The effect of sulphate on aluminium concentrations in natural waters : some stability relations in the system Al_2O_3-SO_3-H_2O at 298K, Geochim. Cosmochim Acta 46, 681-692.

Norton, S.A. & Henriksen, A. (1983) The importance of CO_2 in evaluation of effects of acid deposition, Vatten 39, 346-354.

Paces, T. (1978) Reversible control of aqueous aluminium and silica during the irreversible evolution of natural waters, Geochim. Cosmochim. Acta 42, 1487-1493.

Snodgrass, W.J., Clark, M.M. & O'Melia, C.R. (1984) Particle formation and growth in dilute aluminium (III) solutions. Characterization of particle size distributions at pH 5.5, Water Res. 18, 479-488.

Stumm, W., Kummert, R. & Sigg, L. (1980) A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide surfaces, Croat. Chem. Acta 53, 291-312.

Tanford, C. (1961) Physical Chemistry of Macromolecules. John Wiley and Sons, New York.

Tipping, E., Backes, C.A. & Hurley, M.A. (1988a) The complexation of protons, aluminium and calcium by aquatic humic substances: a model incorporating binding-site heterogeneity and macroionic effects. Water Research, in press.